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(54) Plasma reactor apparatus and method for treating a substrate

Plasma-Reaktionsgerät und Substrat-Behandlungsverfahren

Appareil réacteur à plasma et méthode de traitement d'un substrat

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(56) References cited:
EP-A- 0 090 586 **EP-A- 0 152 511**
WO-A-87/07760 **US-A- 4 767 608**

- **JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART B. vol. 6, no. 1, January 1988, NEW YORK US pages 268 - 271; J Hopwood et al.: "Plasma etching with a microwave cavity plasma disk source"**
- **Journal of Propulsion and Power vol. 3, 1987, pages 136 - 144; S Whitehair et al.: "Microwave electrothermal thruster performance in helium gas"**
- **Plasma Chemistry and Plasma Processing vol. 5, no. 1, 1985, Plenum Publishing Corp. pages 1 - 37; R M Young et al.: "Generation and behavior of fine particles in thermal plasmas - A review"**

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Description

The present invention relates to an improved plasma reactor apparatus with a tunable and electrodeless radiofrequency wave cavity around a confined space for the plasma, and to a method wherein the apparatus and method are used for treating a substrate with an excited species from the plasma in a reaction chamber spaced from the confined space for the plasma.

WO87/07760 discloses an apparatus and a method using a microwave disc plasma and a hybrid plasma to treat surfaces of a substrate. The apparatus includes a quartz tube closed at one end as a plasma confining means, and a reaction chamber for receiving the substrate. The open end of the plasma confining tube is directed to the substrate and is covered by a grid electrically biased to attract ions from the plasma discharge. Slightly above the grid, i.e. the outlet aperture from the confining tube into the reaction chamber, the gas is fed into the plasma confining means resulting in a slightly restricted cross-section within the outlet aperture compared to the cross-section of the confining tube. The apparatus includes a wave coupler defining the mode of resonance and a static magnetic field surrounding the plasma source which aids in coupling electromagnetic energy to plasma electrons at electron cyclotron resonance and aids in confining the charged species in the discharge chamber. The microwave plasma do not impinge onto the substrate, but a further hybrid plasma is ignited immediately above the substrate. This hybrid plasma will then etch the substrate or will form the depositions.

"Journal of Propulsion and Power", vol. 3, 1987, page 136-144, describes a microwave electrothermal thruster having a nozzle as a discharge outlet of the plasma. The known thruster is used for propulsion purposes, and is not described to be used for treating surfaces contained in a reaction chamber.

U.S. Patent Nos. 4,507,588; 4,585,668; 4,727,293; and 4,630,566; describe further methods and apparatus for the generation of an electrodeless disk shaped plasma. The method and apparatus of these patents work very well and are utilized in the present invention, as are the more conventional plasmas formed in elongate quartz tubes as shown in Proceedings of the IEEE 62, 109-117 (1974).

The above referenced patents and publication describe the prior art in great detail. In all of this prior art, a sliding short or other tuning means is used to tune microwaves or other radiofrequency waves in a cavity around the plasma confining means. The sliding short is external of the plasma confining means which is nonmetallic and transparent to the radiofrequency waves (e.g. quartz). Usually the radiofrequency waves are tuned in the cavity so that the reflected power is zero so that the microwaves are resonant and matched in the cavity. Also, radiofrequency waveguides can be used. In this case, the microwaves are propagating in the waveguide. There is an incident wave and a wave is reflected at the plasma discharge. In contrast, a cavity applicator has a resonant standing wave (higher Q) wave incident on the plasma discharge.

In J. of Propulsion and Power 3, 136-144 (1987) and Applied Physics Lett. 44, 1014-1016 (1984) a propulsion device is described. The apparatus includes a nozzle which is used to develop the thrust using a low molecular weight gas (N_2 or He) at high pressures. There was no mention of the device for any materials processing.

One important use of plasmas is in diamond or diamond-like thin film deposition. Such plasma deposition is described for instance in U.S. Patent Nos. 4,471,003, 4,682,564 and 4,487,162 to Cann; U.S. Patent No. 3,961,103 to Aisenberg; U.S. Patent No. 4,647,512 to Venkataramanan et al; U.S. Patent No. 4,060,660 to Carlson et al; U.S. Patent No. 4,663,183 to Ovshinsky et al; U.S. Patent No. 4,728,529 to Etzkorn et al and in U.S. Patent No. 4,434,188 to Kamo et al to produce such films. Some of these patents describe plasmas created by DC arc electrodes which contaminate the coating or the like on the substrate. The electrodes also decrease operating life and increase maintenance. Also Kurihara et al Appl. Phys. Lett 52: 437-438 (1988) describe the use of DC arc plasmas for this purpose. Kamo et al describe an electrodeless plasma apparatus which is an improvement. Also, Kamo et al (M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, Journal of Crystal Growth 62, 642-644 (1983)) show a representative apparatus. Hydrogen and methane are fed into a quartz tube which also contains a substrate on which the diamond film is to be formed. Microwave energy at 2.45 GHz is transmitted to the chamber through a waveguide in order to form a microwave plasma inside the quartz tube. Film growth on the substrate results from chemical vapor deposition as the methane is dissociated into radicals and ions of C and H. With this apparatus, diamond particles were formed on silicon wafers under conditions of 1 to 3% methane, 300 to 700 W of microwave power, and total pressures of approximately 13 to 133 mbar (10 to 100 Torr). The substrate reached temperatures of 800 to 1000°C. There is a need for a method and apparatus which is electrodeless and which can produce a diamond or diamond-like coating over a large surface area at high deposition rates.

U.S. Patent No. 4,767,608 to Matsumoto et al describes the use of plasmas provided through apertures for depositing diamond thin films. No adjustment of the position or size of the plasma relative to the aperture during operation of the apparatus is described. As a result the apparatus is not as versatile and thus can not be adapted to a wide range of processing conditions.

The properties of diamond include an extremely high degree of hardness, a very high thermal conductivity, optical transparency, high electrical resistivity, and semiconductivity induced by doping with trace levels of impurities. The following is a partial list of diamond film applications: lens coating; laser windows; tribology ap-

plications (hard surfaces, long wearing bearings, etc.); electronic packaging and passivation; thermal heat sinks; electrical isolation; high temperature electronic devices; microwave and mm wave power devices; and low noise UV detectors. This unusual combination of properties makes the production of such films highly desirable and a preferred product of the present invention.

Therefore, it is an object of the present invention to provide a method and apparatus for treating substrates with excited species from a plasma wherein films or coatings, for example diamond thin films, can be deposited rapidly and with homogeneity on a large surface. Further still it is an object of the present invention to provide a method which is easy to perform and an apparatus which is simple and economical to construct and operate.

A reactor apparatus and a method designed to comply with this object are described in claims 1 and 16.

Embodiments of the invention are hereinafter described by referring to the figures wherein

Figure 1 is a schematic front cross-sectional view of a plasma reactor apparatus wherein the plasma 15 is confined in a cylindrically cross-sectioned quartz closed end tube 13 adjacent a nozzle 16 and wherein a substrate 17 is mounted on an optionally heated support 18 in a reaction chamber 21 and further showing a sliding short 11 for positioning the plasma 15 during operation of the apparatus.

Figure 1A is a cross-section along line 1A-1A of Figure 1.

Figure 2 is a schematic front cross-sectional view of a plasma reactor apparatus showing the use of a quartz hemisphere 22 for confining the plasma 15a adjacent the nozzle 16 and wherein a substrate 17 is mounted on the support 18 in the reaction chamber 21 and further showing a sliding short 11 for positioning the plasma 15a during operation of the apparatus. Figure 2A is a cross-sectional view along line 2A-2A of Figure 2.

Figure 3 is a schematic front cross-sectional view of a plasma reactor apparatus showing a quartz tube 30 which confines the plasma 31 adjacent a nozzle 32 and wherein a substrate 33 is mounted on a support 34 in a reaction chamber 35 and further showing a sliding short 37 for tuning the plasma 31 during operation of the apparatus. Figure 3A is a cross-sectional view along line 3A-3A of Figure 3.

Figure 4 is a schematic front, cross-sectional view of a preferred apparatus showing dual plasmas 52 and 53 adjacent nozzles 56 and 57 directed at a substrate 59 on an optionally heated support 60 inside a reaction chamber 58 and further showing sliding shorts 64 and 65 for positioning the plasmas 52 and 53 during operation of the apparatus. Figure 4A is a cross-sectional view along line 4A-4A of Figure 4. Figure 4B is a view showing the positioning of the plasma 53 adjacent to the nozzle 57 by means of the sliding short 65.

Figure 5 is a schematic front cross-sectional view of an alternate type of plasma reactor apparatus wherein the cavity 75 is moveable along the axis c-c of a quartz tube 70 confining the plasma 74 in the TM_{012} mode to position the plasma in the tube 70. Figure 5A is a cross-section along line 5A-5A of Figure 5. Figure 5B shows the same thing as Figure 5, except the plasma 74 in tube 70 is in the TM_{011} mode with the discharge in the upper part of tube 70 suppressed.

Figure 6 is a schematic front cross-sectional view of an alternate type of plasma reactor apparatus wherein the tube 80 optionally slides in a quartz receiver 81 along axis d-d to position the plasma 82 in the tube 80 or the cavity 85 can be moved along the axis d-d. Figure 6A is a cross-section along line 6A-6A of Figure 6.

Figure 7 is a schematic front cross-sectional view of another embodiment of a plasma reactor apparatus showing the dual sliding shorts 92 and 93 which position the plasma 94 in the tube 90. Figure 7A is a cross-section along line 7A-7A of Figure 7.

GENERAL DESCRIPTION

The present invention relates to an apparatus for applying a coating to a substrate, comprising: a plasma confining means with an aperture means leading from the plasma confining means; means for introducing a gas into the plasma confining means; means for exciting the plasma confining means with microwave energy to thereby produce a plasma discharge in the plasma confining means; means for adjusting the position of the discharge within the plasma confining means; and means for applying the plasma from the discharge through said aperture means from the plasma confining means to the substrate.

The present invention further relates to a reactor apparatus for exposing a substrate to excited species produced by an electrodeless plasma which comprises: reaction chamber means surrounding and providing a confined space around the substrate which is in the reaction chamber means; radiofrequency wave generating means mounted on the reaction chamber means including a metallic coupler means with a hollow cavity or waveguide for the radiofrequency waves and a tuning means, the coupler means having an opening defining a longitudinal axis directed at the substrate; plasma confining means having a space with a first cross-section between opposed ends in which the plasma is to be generated mounted in the coupler means around the longitudinal axis which is directed at the substrate with an inlet means into the confining means for a gas which is to be converted to a plasma; and aperture means having a second cross-section at one end of the confining means closest to the substrate which is smaller in cross-section than the first cross-section of the confining means and which restricts the flow of the excited species from the plasma into the reaction chamber means and onto the substrate wherein in operation of the apparatus the plasma is created in the space in the confining means and the excited species from the plasma

passes through the aperture means into the chamber means and impinges on the substrate and wherein a plasma positioning means provided on the apparatus is used to position the plasma in the space in the plasma confining means during operation of the apparatus.

Further, the present invention relates to a method for exposing a substrate to excited species from an electrodeless plasma which comprises: providing an apparatus for exposing a substrate to excited species produced by a plasma which comprises: reaction chamber means surrounding and providing a confined space around the substrate which is in the reaction chamber means; radiofrequency wave generating means mounted on the reaction chamber means including a metallic coupler means with a hollow cavity or waveguide for the radiofrequency waves and a tuning means, the coupler means having an opening defining a longitudinal axis directed at the substrate; plasma confining means having a space with a first cross-section between opposed ends in which the plasma is to be generated mounted in the coupler means around the longitudinal axis which is directed at the substrate with an inlet means into the confining means for a gas which is to be converted to a plasma; and aperture means having a second cross-section at one end of the confining means closest to the substrate which is smaller in cross-section than the first cross-section of the confining means and which restricts the flow of the excited species from the plasma into the reaction chamber means and onto the substrate wherein in operation of the apparatus the plasma is created in the space in the confining means and the excited species from the plasma pass through the aperture means into the chamber means and impinge on the substrate; providing a gaseous material in the confining means from the inlet means so as to form the plasma; and exposing the substrate to the excited species from the aperture means, wherein a positioning means provided on the apparatus is used to position the place in the plasma in the space in the plasma confining means during operation of the apparatus.

The "positioning means" for positioning the plasma in the space in the confining means can be a sliding short in the cavity which also functions as a tuning means for the radiofrequency waves; a plasma confining means which is moveable relative to the coupler means or vice versa, and/or a means for varying the power level in the coupler means to change the size or configuration of the plasma. In this manner the plasma ball or disc can be positioned in the space in the plasma confining means as well as expanded or constricted in size. Preferably the plasma is positioned adjacent to the aperture means.

The plasma is formed in a high pressure region and the deposition occurs in a low pressure region. The apparatus and method allows a wide variation of experimental conditions, e.g. by varying the aperture means size and flow rate and input power, different combinations of discharge conditions and thus excited species and deposition conditions in the substrate can be achieved. The aperture means can be variable.

The term "excited species" means electrons and excited states of ions and free radicals. The excited species pass through the aperture and impinge upon the substrate to produce an affect on the substrate.

The term "nozzle" means an aperture which has a constriction and directs the flow of the plasma into the chamber.

The substrate can be provided in the reaction chamber for deposition, etching, oxidation, and other surface treatment. The substrate can be on a support or could be particulate.

The substrate can be provided on a heated support. The support can be heated to temperatures between about 100° and 1000°C. The substrate can also be cooled.

The tuning means, coupler means and confining means can have a variety of configurations. One possible configuration is like the thruster described by Whitehair and Asmussen in Applied Phys. Lett. 10, 1014-1016 (1984).

SPECIFIC DESCRIPTION

Figures 1 and 1A show a microwave metallic cavity 10 with a metallic sliding short or plate 11 including metallic fingers 11a which contact cavity 10. A movable probe 12 is mounted in an inlet 10a to cavity 10. A bottom 10b of the cavity 10 supports a cylindrically shaped quartz closed end tube 13. Magnets 14 are optionally provided around the tube 13 to provide a means for confining and/or generating electron cyclotron resonance at low pressure (below about 100 millitorr) in a plasma 15. At low pressure the plasma fills tube 13. At high pressures the plasma takes on a disk or ball-shaped form as shown. The plasma 15 can also have the orientation shown by the dotted lines. A nozzle 16 (ceramic, such as quartz, or metallic) is provided so that the excited species from the plasma 15 can be directed towards a substrate 17 mounted on a holder or support 18. A radial gas filled conduit 19 is provided to inlet gas into the closed end tube 13. An annular ring 17a with holes 17b is provided to direct the inlet gases. An external coil or coils 20 can be provided around the cavity 10 to create or augment electron cyclotron resonance. The substrate 17 is provided in an enclosed space 21a in reaction chamber 21.

Figures 2 and 2A show a similar apparatus to that shown in Figure 1 except that a quartz hemisphere 22 is used to confine the plasma 15a and there are no magnets.

Figures 3 and 3A show a waveguide applicator with external matching. A gas is provided at an inlet 30a of quartz tube 30 to be used to create a plasma 31. The tube 30 is provided with a nozzle 32 directed at a substrate 33 mounted on a holder or support 34. The substrate 33 is confined in a space 35a in reaction chamber

35. The plasma 31 is created in tube 30 by microwaves in the metallic waveguide 36 which has a metallic sliding short 37 with fingers 37a in contact with an inside surface 36a of waveguide 36. External matching stubs 38, 39 and 40 are provided in ports 37b, 37c and 37d on guide 36. The stubs 38, 39 and 40 and short 37 are used to tune the plasma loaded waveguide to a matched and resonant condition.

In Figures 1 to 3, the plasma excited species from the plasma 15, 15a or 31 passes through the nozzle 16 or 32 and onto the substrate 17 or 33 where a deposit is formed or where the surface is treated as by etching. The closed tube 13, hemisphere 22 or open tube 30 provide a higher pressure space 15b, 15c or 31a for the plasma 15, 15a or 31 to form. The reaction chamber 21 or 35 provides a lower pressure space 21a or 35a for the excited species passing through the nozzle 16 or 32. The sliding short 11 is one means which allows the plasma to be positioned in the tube 13, hemisphere 22 or open tube 30, preferably adjacent to the nozzle 16 or 32. The short 11 also allows tuning of the mode of the plasma. The detailed operation of the apparatus of Figure 1 to 3 is described in further detail by reference to Figure 4.

As depicted in Figures 4, 4a and 4b, the plasma reactor apparatus consists of two microwave discharge applicators 50 and 51. The applicator 50 includes a tube 54 which passes through a space 66a which confines a plasma 52 in cavity 66. The applicator 51 includes a tube 55 which confines plasma 53 which passes through a space 67a in cavity 67. Nozzles 56 and 57 are mounted on tubes 54 and 55, respectively. Slideable shorts 64 and 65 are mounted in the spaces 66a and 67a, respectively, to tune the microwave. Probes 68 and 69 are provided to couple the microwaves into the cavities 66a and 67a, respectively. Excited species from the plasmas 52 and 53 pass through the nozzles 56 and 57 into a common, lower pressure reaction chamber 58 and impinge upon a substrate 59 mounted on a support 60. Applicator 50 has an axis a-a and applicator 51 has an axis b-b directed at the substrate.

The applicators 50 and 51 couple microwave energy into a gas to form the plasmas 52 and 53. The high pressure discharge regions 61 and 62 and a low pressure reaction chamber region 63 are separated by the nozzles 56 and 57. The apparatus produces excited species which pass into the reaction chamber 58 which quenches the excited species such that they do not recombine or de-excite until they reach the reaction surface or substrate 59. Thus the apparatus can be applied to a wide variety of deposition conditions ranging from low pressure molecular beam epitaxy (MBE)--like conditions to high pressure, high rate processes. A specific example of a microwave plasma jet deposition process is the formation of diamond films from methane and hydrogen wherein the hydrogen and methane are in separate applicators 50 and 51.

Input gas flows through the tubes 54 and 55 and into the high pressure regions 61 and 62 and then passes through the nozzles 56 and 57 into the lower pressure region 63. Microwave energy is efficiently coupled into the discharge via the tuned microwave applicators 50 and 51. The pressure differential between the high pressure regions 61 and 62 and low pressure region 63 depends on the nozzle 56 and 57 size, gas type, and gas flow rate. Since microwave plasmas 52 and 53 can be created in the applicators 50 and 51 over a very wide pressure range, gas flow rates vary from more than 10,000 standard cm^3/min (sccm) to less than one standard cm^3/min (sccm). The high flow rates produce a high pressure of 0,5 to 2 bar (1/2 to 2 atmospheres) plasma 52 or 53 while the very low flow rates produce a low pressure plasma 52 or 53 on the order of $1,3 \times 10^{-3}$ mbar (10^{-3} Torr). Thus the apparatus can be employed over a wide range of deposition or reaction conditions. Thus a wide variety of excited species can be introduced into the reaction chamber 58.

Depending on the process, the pressure of the reaction chamber 58 can also be varied over a wide range of conditions. For example, if very low pressure deposition is desired, where the mean free paths of the excited species are long compared to the chamber 58 dimensions ("MBE like" conditions) then very low flow, small nozzles 56 or 57 are utilized and deposition pressures are of the order of $1,3 \times 10^{-6}$ mbar (10^{-6} Torr) or less. In this process, the diameter of the nozzles 56 or 57 is less than one (1) millimeter. If high deposition rates are desired, higher input gas flows and medium to high pressures (up to approximately one bar or one atmosphere) in the reaction chamber 58 are required. By using nozzle 56 or 57 having diameters of 2 to 5 millimeters, discharge pressures can range from hundreds of mbar (Torr) to approximately 2 bar (2 atmospheres).

Preferably the plasma 52 and 53 in each applicator 50 and 51 is positioned adjacent the aperture so that the excited species (i.e. electrons, ions, and excited neutral species) leave the plasma and pass through nozzle 56 and 57 into the chamber 58. Furthermore, when the plasma discharge is placed immediately adjacent to the nozzle 57, as shown by Figure 4B, all of the gas flowing through the tubes 54 and 55 will be excited by the plasmas 52 and 53. This prevents gas from flowing around the plasmas 52 and 53, thereby bypassing the excitation region of the plasmas 52 and 53 and exiting into the reaction chamber 58. With the plasma 52 or 53 in the position shown in Figure 4B, a large number of free radicals are efficiently generated with relatively small amounts of microwave power. Excited species generated within the plasmas 52 and 53 are quickly quenched to a non-equilibrium composition as they rapidly pass into the lower pressure region 63 of the chamber 58.

Figure 4 shows an arrangement where two applicators 50 and 51 inject excited species into the chamber 58 (such as from hydrogen and methane). However, it is also possible to add multiple gases (for example hydrogen and carbon containing compounds) into one ap-

plicator 50 or 51, or to use more than two applicators if more than two components are required for the deposition or to produce uniformity of deposition to increase deposition rate. A single component can be used in each applicator 50 and 51.

Preferably the axes a-a and b-b of the applicators 50 and 51 are about 45° to each other. The axes can be between 10° and 170° from each other.

Port means 58a with valve or closure means 58b can be provided in reaction chamber 58 for introducing gases alone or with particulate materials (not shown). The port means 58a with a valve 58b can also be positioned in the nozzle or adjacent to the nozzle (not shown). The substrate 59 and support 60 can be removed for this method or process.

For diamond thin films, pressures in the reaction chamber 58 greater than 1,3 x 10^{-6} mbar (10^{-6} torr) are used, preferably between 26,7 mbar to 1 bar (20 torr and 1 atmosphere) for high deposition rates. The pressure in the regions 61 and 62 is at least twice that in the reaction chamber 58 or about 53,3 mbar to 2 bar (40 torr to 2 atmospheres).

Figure 5 shows a plasma reactor apparatus wherein a quartz tube 70 is mounted on a processing chamber 71 so as to provide a vacuum seal between the tube 70 and chamber 71. The chamber 71 includes a support 72 for a material 73 to be treated. The axis c-c of tube 70 is directed at the substrate 73. The tube 70 includes a nozzle 70a at one end and a gas inlet 70b at an opposite end. The tube 70 confines a plasma 74 which is excited in the cylindrical cavity TM_{012} mode. The sliding short 77 determines the mode and the position of the plasma 74 in the tube 70. A metallic cavity 75 surrounds the tube 70 and is adjustable in position so that the plasma can be moved to pre-selected positions in the tube 70, preferably adjacent to the nozzle 70a during operation. A probe 76 is used to couple the radiofrequency waves in the cavity 75 and can be adjusted in position.

Figure 5B shows the position of the plasma 74a when excited in the cylindrical cavity TM_{011} mode and is otherwise identical to Figure 5. The cavity 75 in each instance is mounted in order to slide on the tube 70. The cavity 75 can have a separate moveable support means (not shown).

Figures 6 and 6A show another plasma reactor apparatus wherein tube 80 is optionally slideably mounted in a quartz receiver 81 so that the position of plasma 82 relative to nozzle 80a can be changed. Also the cavity 85 can be moved relative to the tube 80. An o-ring (not shown) can be used between the outside of the tube 80 and the inside of the receiver 81. The tube 80 includes a gas inlet 80b. The receiver 81 is mounted in sealed relationship on processing chamber 82 which confines a holder 83 supporting a substrate 84 to be treated. The axis d-d of the tube 80 is directed at the substrate 84. A metallic cavity 85 is used to provide the radiofrequency waves and includes a sliding short 86 which determines the mode and the position of the plasma 82 in the tube 80. By moving the tube 80 in receiver 81, the position of the plasma 82 in tube 80 is determined, preferably adjacent to the nozzle 80a. A probe 87 is used to couple the radiofrequency waves into the cavity 85 and can be adjusted in position.

Figure 7 shows a plasma reactor apparatus wherein a quartz tube 90 is mounted on a receiving chamber (shown in part). The tube 90 has a nozzle 90a and a gas inlet 90b. A metallic radiofrequency wave cavity 91 is provided around the tube 90 and two sliding shorts 92 and 93 are provided in the cavity to position the plasma 94 in the tube 90. Threaded members 92a and 93a are used to move the shorts 92 and 93, respectively. The shorts 92 and 93 provide a relatively easy means for positioning the plasma in the tube 90, preferably adjacent to the nozzle 90a. A probe 95 is used to couple the radiofrequency waves into the cavity 91 which can be adjusted in position. A holder 96 is used to support substrate 97. The axis e-e of the tube 90 is directed at a substrate 97.

The microwave plasma applicator rf the present invention can be used in place of dc and of plasma torches, jets, and thermal plasmas. These include chemical reactions such as nitrodation, production of fine powders, and refining of materials.

Fine particles can be fed into the plasma or into the reaction chamber. ("Generation and Behaviour of Fine Particles in Thermal Plasmas - a Review", R. M. Young and E. Pfender, Plasma Chemistry and Plasma Processing, 5, 1-31, 1985.) Some specific examples are:

(1) high quality powders from low cost materials. These powders are used in powder metallurgy, such as in the production of sintered ceramics. Examples are injecting alumina powder with irregular particle shape and size into the reaction chamber 58 and obtaining spheroidal alumina particles at the output.

(2) the decomposition of metallic ores and oxides. For example, zircon sand can be injected into the reaction chamber 58 and zircon (zirconium silicate) produced. Alumina is injected into plasmas and aluminum is obtained.

(3) introducing aluminum metal particles and adding ammonia to the reaction chamber 58, so that aluminum nitride is obtained. By injecting titanium tetrachloride into the reaction chamber 58, titanium dioxide can be produced which is a white pigment.

(4) Plasma/powder combinations for the production of nitrides, carbides, and borides in the reaction chamber 58.

The apparatus can also be used for surface treating metals, such as nitridation of titanium. ("Nitriding of Titanium with Plasma Jet Under Reduced Pressure", O. Matsumoto, et al., Plasma Chemistry and Plasma Processing, 4, 33-42, 1984.)

The plasma applicator can also be used for sputtering applications. In one instance a beam would impinge upon a target to remove particles which deposit on another surface. A particulate material could also be used for the target.

The plasma confining means are made from a material transparent to microwaves, but capable of withstanding high temperatures. Examples of suitable materials are quartz and boron nitride. Nozzles are made of materials which are the same as the plasma confining means or of materials which are not necessarily transparent to microwaves. Examples of the latter materials are stainless steel, graphite and copper.

It is intended that the foregoing description be only illustrative of the present invention and that the present invention be limited only by the hereinafter appended claims.

Claims

1. A reactor apparatus for exposing a substrate (17, 33, 59, 73, 84, 97) to excited species produced by an electrodeless plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) which comprises:

    reaction chamber means (21, 35, 58, 71, 82) surrounding and providing a confined space around the substrate which is in the reaction chamber means; radiofrequency wave generating means mounted on the reaction chamber means (21, 35, 58, 71, 82) including a metallic coupler means with a hollow cavity (10, 66, 67, 75, 85, 91) or a waveguide (36) for the radiofrequency waves and a tuning means (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93), the coupler means having an opening defining a longitudinal axis (a-a, b-b, c-c, d-d, e-e) directed at the substrate;

    plasma confining means (13, 22, 30, 54, 55, 70, 80, 90) having a space with a first cross-section between opposed ends in which the plasma is to be generated mounted in the coupler means around the longitudinal axis (a-a, b-b, c-c, d-d, e-e) which is directed at the substrate, said plasma confining means having an inlet means (19, 30a, 70b, 80b, 90b) for introducing into the confining means at a predetermined gas flow rate a gas which is to be converted to the plasma; and

    nozzle means (16, 32, 56, 57, 70a, 80a, 90a) connecting one end of the plasma confining means closest to the substrate to the reaction chamber means, said nozzle means consisting of a single aperture which opens into the reaction chamber means by a funnel shaped member, the aperture being arranged coaxially to the longitudinal axis and having a second cross-section which is smaller in cross-section than the first cross-section of the confining means so that the nozzle means (16, 32, 56, 57, 70a, 80a, 90a) restricts the flow of the excited species from the plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) into the reaction chamber means (21, 35, 58, 71, 82) and onto the substrate (17, 33, 59, 73, 84, 97) such that a pressure differential between a high pressure region (15b, 15c, 31a, 61, 62) of said confining means and a low pressure region (21a, 35a, 63) of said reaction chamber is created depending on the type of said gas and said predetermined gas flow rate, the pressure in the high pressure region being at least twice that of the low pressure region, wherein in operation of the apparatus the plasma is created in the space in the confining means (13, 22, 30, 54, 55, 70, 80, 90) and the excited species from the plasma passes through the nozzle means (16, 32, 56, 57, 70a, 80a, 90a) into the reaction chamber means and impinges on the substrate and wherein a plasma positioning means (11, 37, 64, 65, 77, 81, 86, 92, 93) provided on the apparatus is used to position the plasma relative to said nozzle means along the axis (a-a, b-b, c-c, d-d, e-e) in the plasma confining means during operation of the apparatus.

2. The apparatus of claim 1 wherein two or more of the radiofrequency wave generating means with the confining means (54, 55) and nozzle means (56, 57) are mounted on the reaction chamber means (58) each with the longitudinal axis directed at the substrate (59).

3. The apparatus of claim 1 or 2 wherein the wave generating means can be adjusted in input power to the coupler means (10, 66, 67, 75, 85, 91) or waveguide (36) and the inlet means (19, 30a, 70b, 80b, 90b) can be adjusted in flow rate of the gas so as to vary the excited species which impinge on the substrate (17, 33, 59, 73, 84, 97).

4. The apparatus of claim 2 or 3 wherein there are two radiofrequency wave generating means (50, 51) and wherein the axes are at an angle between about 10° and 170° to each other and directed at the substrate (59).

5. The apparatus of claim 4 wherein the angle is about 45°.

6. The apparatus of any one of claims 1 to 5 wherein the confining means (13, 30, 54, 55, 70, 80, 90) is a tube and the cross-section is circular.

7. The apparatus of any one of claims 1 to 6 wherein port means (58a) is provided for introducing a particulate solid material as the substrate into the reaction chamber (58) for treatment by the excited species.

8. The apparatus of any one of claims 1 to 7 wherein the tuning means (11, 64, 65, 77, 86, 92, 93) is inside the cavity (10, 66, 67, 75, 85, 91).

9. The apparatus of any one of claims 1 to 7 wherein the tuning means (38, 39, 40) is external of the cavity or waveguide (36).

10. The apparatus of any one of claims 1 to 9 wherein in use of the apparatus the plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) is positioned adjacent to the nozzle means (16, 32, 56, 57, 70a, 80a, 90a).

11. The apparatus of any one of claims 1 to 10 wherein said tuning means includes a movable plate means (11, 64, 65, 77, 86, 92, 93) closing the coupler means at one end which is movable perpendicular to the axis in contact with the surface of the cavity (10, 66, 67, 75, 85, 91).

12. The apparatus of claim 11 wherein the movable plate means (11, 64, 65, 77, 86, 92, 93) is used to position the plasma in the space in the confining means during operation of the apparatus.

13. The apparatus of any one of claims 1 to 12 wherein the plasma confining means (70, 80) and the cavity (75, 85) for excitation of the plasma are movable relative to each other.

14. The apparatus of any one of claims 1 to 13 wherein more than one of the means (77, 81, 86, 92, 93) for adjusting the position of the plasma are provided for adjusting the position of the plasma in the plasma confining means (70, 80, 90).

15. The apparatus of any one of claims 1 to 14 including a holder means (18, 34, 60, 72, 83, 96) for supporting the substrate onto which the material is to be deposited.

16. A method for exposing a substrate (17, 33, 59, 73, 84, 97) to excited species from an electrodeless plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) which comprises:
providing an apparatus for exposing a substrate to excited species produced by a plasma which comprises: reaction chamber means (21, 35, 58, 71, 82) surrounding and providing a confined space around the substrate which is in the reaction chamber means; radiofrequency wave generating means mounted on the reaction chamber means including a metallic coupler means with a hollow cavity (10, 66, 67, 75, 85, 91) or a waveguide (36) for the radiofrequency waves and a tuning means (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93), the coupler means having an opening defining a longitudinal axis (a-a, b-b, c-c, d-d, e-e) directed at the substrate; plasma confining means (13, 22, 30, 54, 55, 70, 80, 90) having a space with a first cross-section between opposed ends in which the plasma is to be generated mounted in the coupler means around the longitudinal axis (a-a, b-b, c-c, d-d, e-e) directed at the substrate, said plasma confining means having an inlet means (19, 30a, 70b, 80b, 90b) for introducing into the confining means a gas at a predetermined **gas** flow **rate**; and a nozzle means (16, 32, 56, 57, 70a, 80a, 90a) connecting one end of the plasma confining means close to the substrate to the reaction chamber means, said nozzle means is formed of a single aperture which opens into the reaction chamber means by a funnel shaped member, the aperture being arranged coaxially to the longitudinal axis and having a second cross-section which is smaller in cross-section than the first cross-section of the confining means; and providing a gaseous material in the confining means from the inlet means so as to form the plasma;
and comprises the steps of
restricting the flow of the excited species from the plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) into the reaction chamber means (21, 35, 58, 71, 82) and onto the substrate (17, 33, 59, 73, 84, 97) by said nozzle means (16, 32, 56, 57, 70a, 80a, 90a) for creating a pressure differential between a high pressure region (15b, 15c, 31a, 61, 62) of said confining means and a low pressure region (21a, 35a, 63) of said reaction chamber depending on the type of said gas and said predetermined gas flow rate, such that the pressure in the high pressure region being at least twice that of the low pressure wherein in operation of the apparatus the plasma is created in the space in the confining means (13, 22, 30, 54, 55, 70, 80, 90) and the excited species from the plasma pass through the nozzle means into the reaction chamber means and impinge on the substrate; and exposing the substrate to the excited species from the nozzle means, wherein a plasma positioning means (11, 37, 64, 65, 77, 81, 86, 92, 93) provided on the apparatus is used to position the plasma relative to said nozzle means along the axis (a-a, b-b, c-c, d-d, e-e) in the space in the confining means during operation of the apparatus.

Patentansprüche

1. Reaktorvorrichtung zum Aussetzen eines Substrates (17, 33, 59, 73, 84, 97) den durch ein elektrodenloses Plasma (15, 15a, 31, 52, 53, 74, 74a, 82,

94) produzierten, angeregten Bestandteilen mit:

einer Reaktionskammereinrichtung (21, 35, 58, 71, 82), die das in der Reaktionskammereinrichtung befindliche Substrat umgibt und einen abgeschlossenen Raum darum bildet; einer Erzeugungseinrichtung für Radiofrequenzwellen, die an der Reaktionskammereinrichtung (21, 35, 58, 71, 82) montiert ist, und einer metallischen Koppeleinrichtung mit einem Hohlraum (10, 66, 67, 75, 85, 91) oder mit einem Wellenleiter (36) für die Radiofrequenzwellen und einer Tunereinrichtung (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93); wobei die Koppeleinrichtung eine Öffnung hat, die eine auf das Substrat gerichtete Längsachse (a-a, b-b, c-c, d-d, e-e) definiert;

einer Plasma-Einschließungseinrichtung (13, 22, 30, 54, 55, 70, 80, 90) mit einem Raum mit einem ersten Querschnitt zwischen einander gegenüberliegenden Enden, in dem das Plasma erzeugt wird, die in der Koppeleinrichtung um die auf das Substrat gerichtete Längsachse (a-a, b-b, c-c, d-d, e-e) montiert ist, wobei die Plasma-Einschließungseinrichtung eine Einlaßeinrichtung (19, 30a, 70b, 80b, 90b) zum Eintrag eines Gases, das in das Plasma umgewandelt werden soll, in die Einschließungseinrichtung unter einer vorbestimmten Gasströmungsgeschwindigkeit; und

einer Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a), die ein Ende der Plasma-Einschließungseinrichtung, das dem Substrat am nächsten ist, mit der Reaktionskammereinrichtung verbindet, wobei die Düseneinrichtung aus einer einzigen Öffnung besteht, die sich in die Reaktionskammereinrichtung durch ein trichterförmig geformtes Teil öffnet, wobei die Öffnung koaxial mit der Längsachse ausgerichtet ist und eine zweite Querschnittsfläche hat, die im Querschnitt kleiner ist als die erste Querschnittsfläche der Einschließungseinrichtung, so daß die Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a) die Strömung der angeregten Bestandteile aus dem Plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) in die Reaktionskammereinrichtung (21, 35, 58, 71, 82) und auf das Substrat (17, 33, 59, 73, 84, 97) beschränkt, so daß eine Druckdifferenz zwischen einem Hochdruckbereich (15c, 15b, 31a, 61, 62) der Einschließungseinrichtung und einem Niedrigdruckbereich (21a, 35a, 63) der Reaktionskammer erzeugt wird, in Abhängigkeit von der Art des Gases und der vorbestimmten Gasströmungsrate, wobei der Druck im Hochdruckbereich mindestens doppelt so groß ist als im Niedrigdruckbereich, wobei im Betrieb der Vorrichtung das Plasma im Raum in der Einschließungseinrichtung (13, 22, 30, 54, 55, 70, 80, 90) erzeugt wird und die angeregten Bestandteile aus dem Plasma durch die Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a) in die Reaktionskammereinrichtung hindurchtreten und auf das Substrat aufprallen, und wobei eine an der Vorrichtung vorgesehene Plasma-Positioniereinrichtung (11, 37, 64, 65, 77, 81, 86, 92, 93) verwendet ist, um das Plasma relativ zur Düseneinrichtung entlang der Achse (a-a, b-b, c-c, d-d, e-e) in der Plasma-Einschließungseinrichtung während des Betriebs der Vorrichtung zu positionieren.

2. Vorrichtung nach Anspruch 1, daß zwei oder mehr Erzeugungseinrichtungen für Radiofrequenzwellen mit der Einschließungseinrichtung (54, 55) und der Düseneinrichtung (56, 57) an der Reaktionskammereinrichtung (58) jeweils mit der auf das Substrat (59) ausgerichteten Achse montiert sind.

3. Vorrichtung nach Anspruch 1 oder 2, wobei die Wellenerzeugungseinrichtung hinsichtlich der Eintragsenergie in die Kopplereinrichtung (10, 66, 67, 75, 85, 81) oder dem Wellenleiter (36) einstellbar ist, und die Einlaßeinrichtung (19, 30a, 70b, 80b, 90b) hinsichtlich der Strömungsrate des Gases eingestellt werden kann, um die angeregten Bestandteile, die auf das Substrat (17, 33, 59, 73, 84, 97) aufprallen, zu verändern.

4. Vorrichtung nach Anspruch 2 oder 3, wobei es zwei Radiofrequenzwellen-Erzeugungseinrichtungen (50, 51) gibt, und wobei die Achsen unter einem Winkel zwischen etwa 10° und 170° zueinander angeordnet und auf das Substrat (59) gerichtet sind.

5. Vorrichtung nach Anspruch 4, wobei der Winkel etwa 45° beträgt.

6. Vorrichtung nach einem der Ansprüche 1 bis 5, wobei die Einschließungseinrichtung (13, 30, 54, 55, 70, 80, 90) eine Röhre ist, und die Querschnittsfläche kreisförmig ist.

7. Vorrichtung nach einem der Ansprüche 1 bis 6, wobei eine Öffnungseinrichtung (58a) vorgesehen ist, um partikelförmiges festes Material als Substrat in die Reaktionskammer (58) für eine Behandlung mit den angeregten Bestandteilen einzuleiten.

8. Vorrichtung nach einem der Ansprüche 1 bis 7, wobei die Tunereinrichtung (11, 64, 65, 77, 86, 92, 93) sich innerhalb des Hohlraums (11, 66, 67, 75, 85, 91) befindet.

9. Vorrichtung nach einem der Ansprüche 1 bis 7, wobei die Tunereinrichtung (38, 39, 40) außerhalb des Hohlraums oder des Wellenleiters (36) angeordnet ist.

10. Vorrichtung nach einem der Ansprüche 1 bis 9, wobei bei Benutzung der Vorrichtung das Plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) benachbart der Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a) angeordnet ist.

11. Vorrichtung nach einem der Ansprüche 1 bis 10, wobei die Tunereinrichtung eine bewegbare Platteneinrichtung (11, 64, 65, 77, 86, 92, 93) aufweist, die die Kopplereinrichtung an einem Ende verschließt und rechtwinklig zur Achse in Kontakt mit der Oberfläche des Hohlraums (10, 66, 67, 75, 85, 91) bewegbar ist.

12. Vorrichtung nach Anspruch 11, wobei die bewegbare Platteneinrichtung (11, 64, 65, 77, 86, 92, 93) verwendet wird, um das Plasma im Raum in der Einschließungseinrichtung während des Betriebs der Vorrichtung zu positionieren.

13. Vorrichtung nach einem der Ansprüche 1 bis 12, wobei die Plasma-Einschließungseinrichtung (70, 80) und der Hohlraum (75, 85) zum Erregen des Plasmas relativ zueinander bewegbar sind.

14. Vorrichtung nach einem der Ansprüche 1 bis 13, wobei mehr als eine Einrichtung (77, 81, 86, 92, 93) zum Einstellen der Position des Plasmas vorgesehen sind, um die position des Plasmas in der Plasma-Einschließungseinrichtung (70, 80, 90) einzustellen.

15. Vorrichtung nach einem der Ansprüche 1 bis 14, umfassend eine Haltereinrichtung (18, 34, 60, 72, 83, 96), zum Unterstützen des Substrates auf dem das Material abgelagert werden soll.

16. Verfahren zum Aussetzen eines Substrates (17, 33, 59, 73, 84, 97) den angeregten Bestandteilen eines elektrodenlosen Plasmas (15, 15a, 31, 52, 53, 74, 74a, 82, 94) umfassend:

das Schaffen einer Vorrichtung zum Aussetzen eines Substrates den durch ein Plasma produzierten, angeregten Bestandteilen, die umfaßt: eine Reaktionskammereinrichtung (21, 35, 58, 71, 82), die das sich in der Reaktionskammereinrichtung befindende Substrat umschließt und einen abgeschlossenen Raum darum bildet; eine Erzeugungseinrichtung für Radiofrequenzwellen, die an der Reaktionskammereinrichtung montiert ist, und eine metallische Kopplereinrichtung, die einen Hohlraum (10, 66, 67, 75 85, 91) oder einen Wellenleiter (36) für die Radiofrequenzwellen sowie einen Tuner (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93) umfaßt, wobei die Kopplereinrichtung eine Öffnung hat, die eine auf das Substrat gerichtete Längsachse (a-a, b-b, c-c, d-d, e-e) definiert; eine Plasma-Einschließungseinrichtung (13, 22, 30, 54, 55, 70, 80, 90) mit einem Raum mit einem ersten Querschnitt zwischen benachbarten Enden, in dem das Plasma erzeugt wird, und die in der Kopplereinrichtung um die auf das Substrat gerichtete Längsachse (a-a, b-b, c-c, d-d, e-e) montiert ist, wobei die Plasma-Einschlie-ßungseinrichtung eine Einlaßeinrichtung (19, 30a, 70b, 80b, 90b) für das Einbringen eines Gases in die Einschließungseinrichtung unter einer vorbestimmten Gasströmungsrate hat; und eine Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a), die ein Ende der Plasma-Einschließungseinrichtung, die dem Substrat am nächsten ist, mit der Reaktionskammereinrichtung verbindet, wobei die Düseneinrichtung aus einer einzigen Öffnung gebildet ist, die sich in die Reaktionskammer durch ein trichterförmiges Teil öffnet, wobei die Öffnung koaxial zur Längsachse angeordnet ist, und eine zweite Querschnittsfläche aufweist, die im Querschnitt schmaler ist als die erste Querschnittsfläche der Einschließungseinrichtung, und durch Vorsehen eines gasförmigen Materials in der Einschließungseinrichtung von der Einlaßeinrichtung, um ein Plasma zu bilden; und enthaltend die Verfahrensschritte des

Beschränkens der Strömung der angeregten Bestandteile aus dem Plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) in die Reaktionskammereinrichtung (21, 35, 58, 71, 82) und auf das Substrat (17, 33, 59, 73, 84, 97) durch die Düseneinrichtung (16, 32, 56, 57, 70a, 80a, 90a) zum Erzeugen einer Druckdifferenz zwischen einem Hochdruckbereich (15b, 15c, 31a, 61, 62) der Einschließungseinrichtung und einem Niedrigdruckbereich (21a, 35a, 63) der Reaktionskammer, in Abhängigkeit von der Art des Gases und der vorbestimmten Gasströmungsrate, so daß der Druck im Hochdruckbereich mindestens doppelt so groß ist wie der niedrige Druck, wobei beim Betrieb der Vorrichtung das Plasma im Raum in der Einschließungseinrichtung (13, 22, 30, 54, 55, 70, 80, 90) erzeugt wird und die angeregten Bestandteile aus dem Plasma durch die Düseneinrichtung in die Reaktionskammereinrichtung hindurchtreten, und auf dem Substrat aufprallen; und des Aussetzens des Substrates den angeregten Bestandteilen aus der Düseneinrichtung, wobei eine Plasma-Positioniereinrichtung (11, 37, 64, 65, 77, 81,

86, 92, 93), die an der Vorrichtung vorgesehen ist, vervendet wird, um das Plasma relativ zur Düseneinrichtung entlang der Achse (a-a, b-b, c-c, d-d, e-e) im Raum in der Einschließungseinrichtung während des Betriebs der Vorrichtung zu positionieren.

Revendications

1. Appareil de réacteur pour exposer un substrat (17, 33, 59, 73, 84, 97) à des espèces excitées produites par un plasma sans électrode (15, 15a, 31, 52, 53, 74, 74a, 82, 94) qui comprend :

   des moyens de chambre de réaction (21, 35, 58, 71, 82) entourant et réalisant un espace confiné autour du substrat qui se trouve dans les moyens de chambre de réaction ; des moyens de production d'onde de fréquence radioélectrique montés sur les moyens de chambre de réaction (21, 35, 58, 71, 82) incluant des moyens de coupleur métallique avec une cavité creuse (10, 66, 67, 75, 85, 91) ou un guide d'ondes (36) pour les ondes de fréquence radioélectrique et des moyens d'accord (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93), les moyens de coupleur ayant une ouverture définissant un axe longitudinal (a-a, b-b, c-c, d-d, e-e) orienté vers le substrat ;
   des moyens de confinement de plasma (13, 22, 30, 54, 55, 70, 80, 90) comportant un espace ayant une première section transversale entre des extrémités opposées dans lequel le plasma est à produire, montés dans les moyens de coupleur autour de l'axe longitudinal (a-a, b-b, c-c, d-d, e-e) qui est orienté vers le substrat, lesdits moyens de confinement de plasma possédant des moyens d'entrée (19, 30a, 70b, 80b, 90b) pour introduire dans les moyens de confinement, à une vitesse d'écoulement de gaz prédéterminée, un gaz qui est à transformer en plasma ; et
   des moyens de buse (16, 32, 56, 57, 70a, 80a, 90a) reliant une extrémité particulière des moyens de confinement de plasma, la plus proche du substrat, aux moyens de chambre de réaction, lesdits moyens de buse étant constitués par une unique ouverture qui s'ouvre dans les moyens de chambre de réaction par un élément en forme d'entonnoir, l'ouverture étant agencée de manière coaxiale par rapport à l'axe longitudinal et ayant une seconde section transversale qui est plus petite en section transversale que la première section transversale des moyens de confinement de sorte que les moyens de buse (16, 32, 56, 57, 70a, 80a, 90a) limitent l'écoulement des espèces excitées en provenance du plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) dans les moyens de chambre de réaction (21, 35, 58, 71, 82) et sur le substrat (17, 33, 59, 73, 84, 97) de sorte qu'un différentiel de pression, entre une zone de haute pression (15b, 15c, 31a, 61, 62) desdits moyens de confinement et une zone de basse pression (21a, 35a, 63) de ladite chambre de réaction, est créé en fonction du type dudit gaz et de ladite vitesse d'écoulement de gaz prédéterminée, la pression dans la zone de haute pression étant au moins égale à deux fois celle de la zone de basse pression, dans lequel, dans la mise en oeuvre de l'appareil, le plasma est créé dans l'espace des moyens de confinement (13, 22, 30, 54, 55, 70, 80, 90) et les espèces excitées en provenance du plasma passent à travers les moyens de buse (16, 32, 56, 57, 70a, 80a, 90a) dans les moyens de chambre de réaction et viennent heurter le substrat, et dans lequel des moyens de positionnement de plasma (11, 37, 64, 65, 77, 81, 86, 92, 93), disposés sur l'appareil, sont utilisés pour positionner le plasma par rapport auxdits moyens de buse le long de l'axe (a-a, b-b, c-c, d-d, e-e) dans les moyens de confinement de plasma pendant la mise en oeuvre de l'appareil.

2. Appareil selon la revendication 1, dans lequel deux ou plus des moyens de production d'onde de fréquence radioélectrique, avec les moyens de confinement (54, 55) et les moyens de buse (56, 57), sont montés sur les moyens de chambre de réaction (58), chacun avec l'axe longitudinal orienté vers le substrat (59).

3. Appareil selon la revendication 1 ou 2, dans lequel les moyens de production d'onde peuvent être réglés en ce qui concerne la puissance d'entrée dans les moyens de coupleur (10, 66, 67, 75, 85, 91) ou dans le guide d'ondes (36) et les moyens d'entrée (19, 30a, 70b, 80b, 90b) peuvent être réglés en ce qui concerne la vitesse d'écoulement du gaz de façon à faire varier les espèces excitées qui viennent heurter le substrat (17, 33, 59, 73, 84, 97).

4. Appareil selon la revendication 2 ou 3, dans lequel il y a deux moyens de production d'onde de fréquence radioélectrique (50, 51) et dans lequel les axes sont à un certain angle entre environ 10° et 170° l'un par rapport à l'autre et orientés vers le substrat (59).

5. Appareil selon la revendication 4, dans lequel l'angle est d'environ 45°.

6. Appareil selon l'une quelconque des revendications 1 à 5, dans lequel les moyens de confinement (13,

30, 54, 55, 70, 80, 90) sont un tube et la section transversale est circulaire.

7. Appareil selon l'une quelconque des revendications 1 à 6, dans lequel des moyens d'orifice (58a) sont prévus pour introduire une matière solide en particules en tant que substrat dans la chambre de réaction (58) pour un traitement par les espèces excitées.

8. Appareil selon l'une quelconque des revendications 1 à 7, dans lequel les moyens d'accord (11, 64, 65, 77, 86, 92, 93) se situent à l'intérieur de la cavité (10, 66, 67, 75, 85, 91).

9. Appareil selon l'une quelconque des revendications 1 à 7, dans lequel les moyens d'accord (38, 39, 40) sont à l'extérieur de la cavité ou du guide d'ondes (36).

10. Appareil selon l'une quelconque des revendications 1 à 9, dans lequel, lors de l'utilisation de l'appareil, le plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) est positionné à côté des moyens de buse (16, 32, 56, 57, 70a, 80a, 90a).

11. Appareil selon l'une quelconque des revendications 1 à 10, dans lequel lesdits moyens d'accord comprennent des moyens de plaque mobile (11, 64, 65, 77, 86, 92, 93) fermant les moyens de coupleur au niveau d'une extrémité particulière qui est mobile perpendiculairement à l'axe en contact avec la surface de la cavité (10, 66, 67, 75, 85, 91).

12. Appareil selon la revendication 11, dans lequel les moyens de plaque mobile (11, 64, 65, 77, 86, 92, 93) sont utilisés pour positionner le plasma dans l'espace dans les moyens de confinement pendant la mise en oeuvre de l'appareil.

13. Appareil selon l'une quelconque des revendications 1 à 12, dans lequel les moyens de confinement de plasma (70, 80) et la cavité (75, 85) pour l'excitation du plasma sont mobiles les uns par rapport aux autres.

14. Appareil selon l'une quelconque des revendications 1 à 13, dans lequel plus d'un moyen des moyens (77, 81, 86, 92, 93) pour régler la position du plasma, est prévu pour régler la position du plasma dans les moyens de confinement de plasma (70, 80, 90).

15. Appareil selon l'une quelconque des revendications 1 à 14, comprenant des moyens de support (18, 34, 60, 72, 83, 96) pour supporter le substrat sur lequel la matière est à déposer.

16. Procédé pour exposer un substrat (17, 33, 59, 73, 84, 97) à des espèces excitées en provenance d'un plasma sans électrode (15, 15a, 31, 52, 53, 74, 74a, 82, 94) qui comprend :

la fourniture d'un appareil pour exposer un substrat à des espèces excitées produites par un plasma qui comprend : des moyens de chambre de réaction (21, 35, 58, 71, 82) entourant et réalisant un espace confiné autour du substrat qui se trouve dans les moyens de chambre de réaction ; des moyens de production d'onde de fréquence radioélectrique montés sur les moyens de chambre de réaction incluant des moyens de coupleur métallique avec une cavité creuse (10, 66, 67, 75, 85, 91) ou un guide d'ondes (36) pour les ondes de fréquence radioélectrique et des moyens d'accord (11, 37, 38, 39, 40, 64, 65, 77, 86, 92, 93), les moyens de coupleur ayant une ouverture définissant un axe longitudinal (a-a, b-b, c-c, d-d, e-e) dirigé vers le substrat ; des moyens de confinement de plasma (13, 22, 30, 54, 55, 70, 80, 90) comportant un espace ayant une première section transversale entre des extrémités opposées dans lequel le plasma est à produire, montés dans les moyens de coupleur autour de l'axe longitudinal (a-a, b-b, c-c, d-d, e-e) dirigé vers le substrat, lesdits moyens de confinement de plasma possédant des moyens d'entrée (19, 30a, 70b, 80b, 90b) pour introduire un gaz dans les moyens de confinement, à une vitesse d'écoulement prédéterminée ; et des moyens de buse (16, 32, 56, 57, 70a, 80a, 90a) reliant une extrémité particulière des moyens de confinement de plasma, la plus proche du substrat, aux moyens de chambre de réaction, lesdits moyens de buse étant constitués par une unique ouverture qui s'ouvre dans les moyens de chambre de réaction par un élément en forme d'entonnoir, l'ouverture étant agencée de manière coaxiale par rapport à l'axe longitudinal et ayant une seconde section transversale qui est plus petite en section transversale que la première section transversale des moyens de confinement ; et la fourniture d'une matière gazeuse dans les moyens de confinement à partir des moyens d'entrée de façon à former le plasma ;

et comprend les étapes suivantes

la limitation de l'écoulement des espèces excitées en provenance du plasma (15, 15a, 31, 52, 53, 74, 74a, 82, 94) dans les moyens de chambre de réaction (21, 35, 58, 71, 82) et sur le substrat (17, 33, 59, 73, 84, 97) par lesdits moyens de buse (16. 32, 56, 57, 70a, 80a, 90a) pour créer un différentiel de pression, entre une zone de haute pression (15b, 15c, 31a, 61, 62) desdits moyens de confinement et une zone de basse pression (21a, 35a, 63) de ladite chambre de réaction, en fonction du type dudit gaz et de ladite vitesse d'écoulement de gaz prédéterminée, de sorte que la pression dans la zone de haute pression soit au moins égale à

deux fois celle de la zone de basse pression, dans lequel, dans la mise en oeuvre de l'appareil, le plasma est créé dans l'espace des moyens de confinement (13, 22, 30, 54, 55, 70, 80, 90) et les espèces excitées en provenance du plasma passent à travers les moyens de buse dans les moyens de chambre de réaction et viennent heurter le substrat ; et l'exposition du substrat aux espèces excitées en provenance des moyens de buse, dans lequel des moyens de positionnement de plasma (11, 37, 64, 65, 77, 81, 86, 92, 93), disposés sur l'appareil, sont utilisés pour positionner le plasma par rapport auxdits moyens de buse le long de l'axe (a-a, b-b, c-c, d-d, e-e) dans l'espace dans les moyens de confinement pendant la mise en oeuvre de l'appareil.

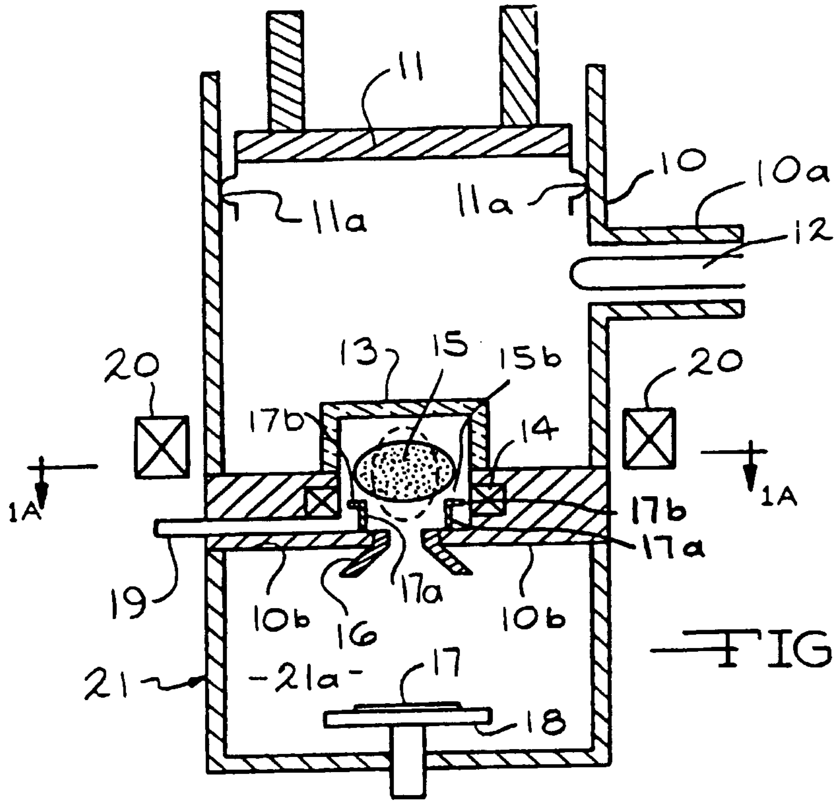

11
10
10a
11a
11a
12
13
15
15b
20
20
17b
14
1A
1A
17b
17a
19
10b
16
17a
10b
21
-21a-
17
18

FIG 1

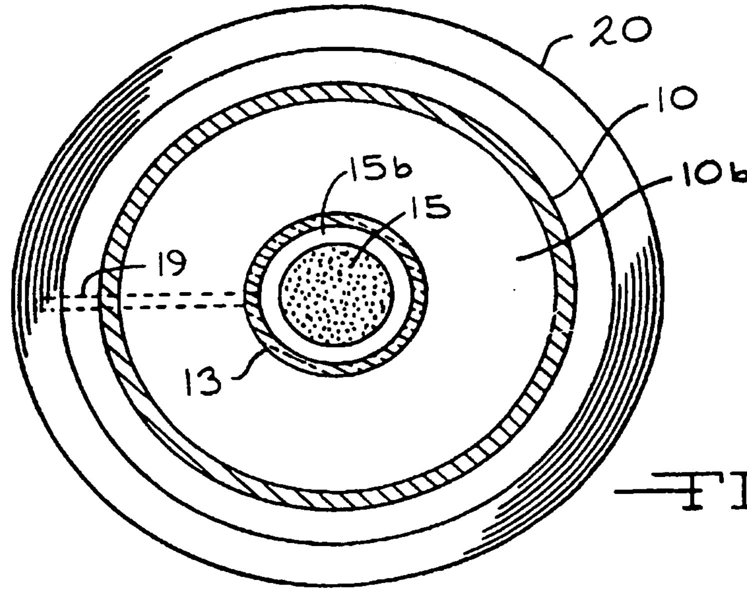

20
10
15b
10b
15
19
13

FIG. 1A

EP 0 388 800 B1

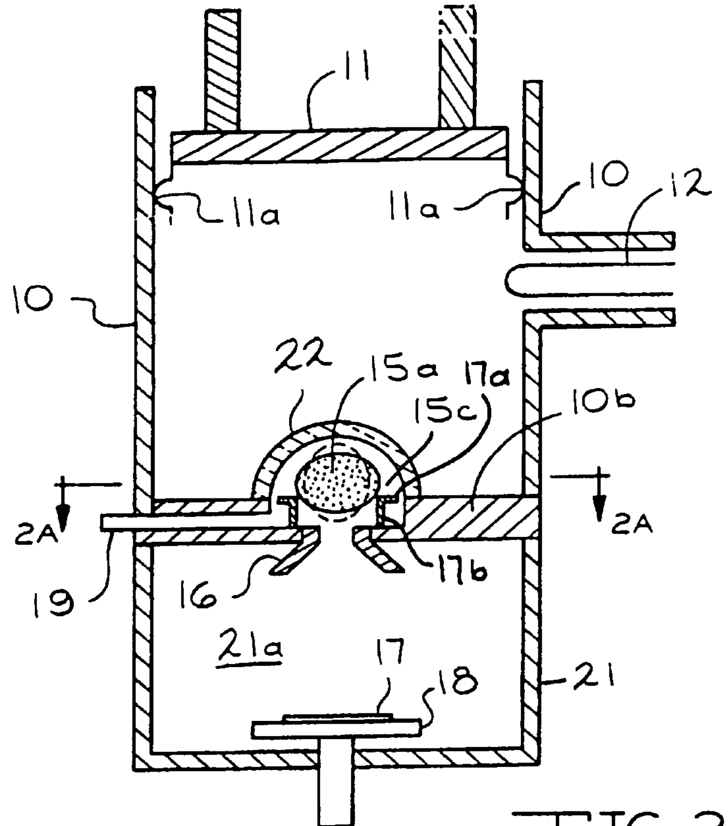


FIG. 2

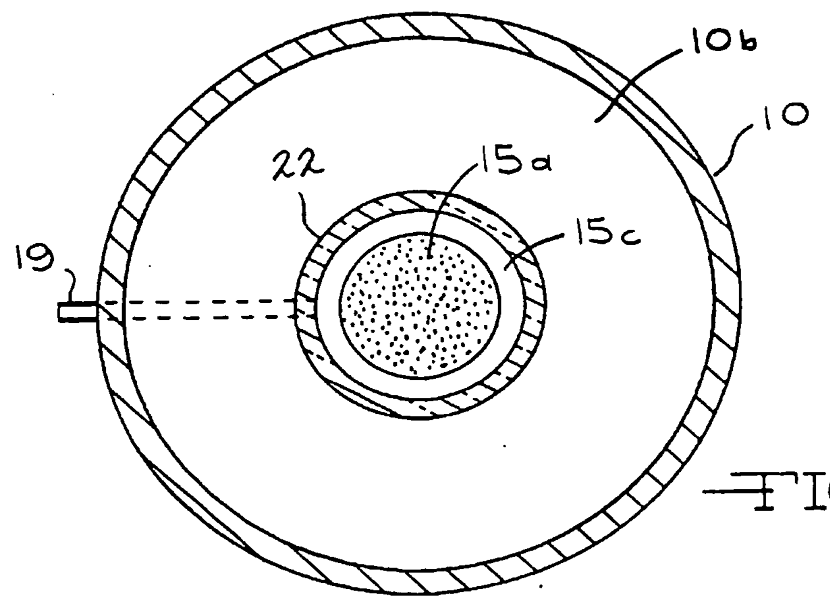


FIG. 2A

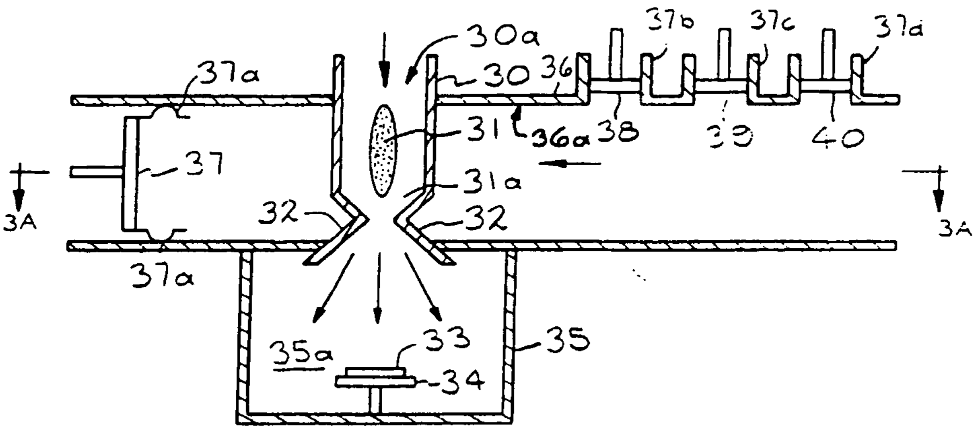

30a
37b
37c
37d
37a
30
36
31
36a
38
39
40
37
31a
3A
32
32
3A
37a
35a
33
35
34

FIG. 3

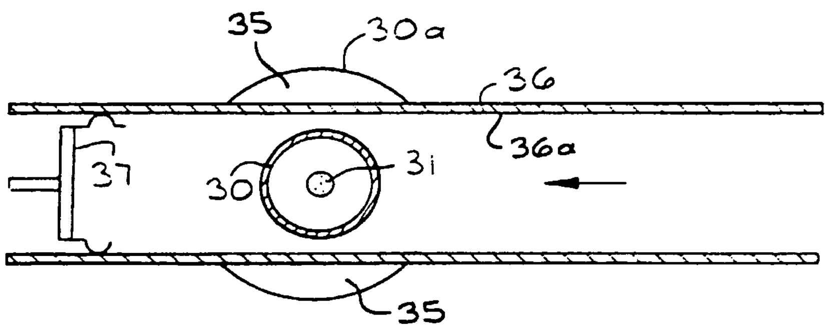

35
30a
36
37
36a
30
31
35

FIG. 3A

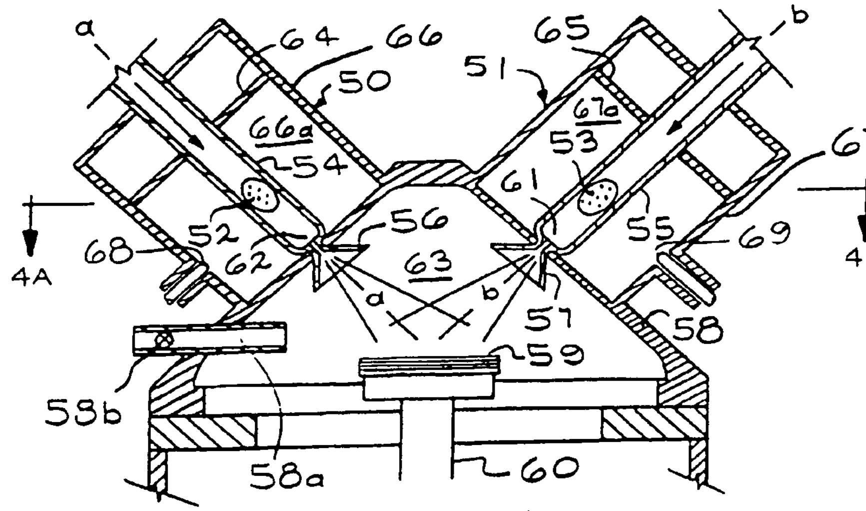


FIG. 4

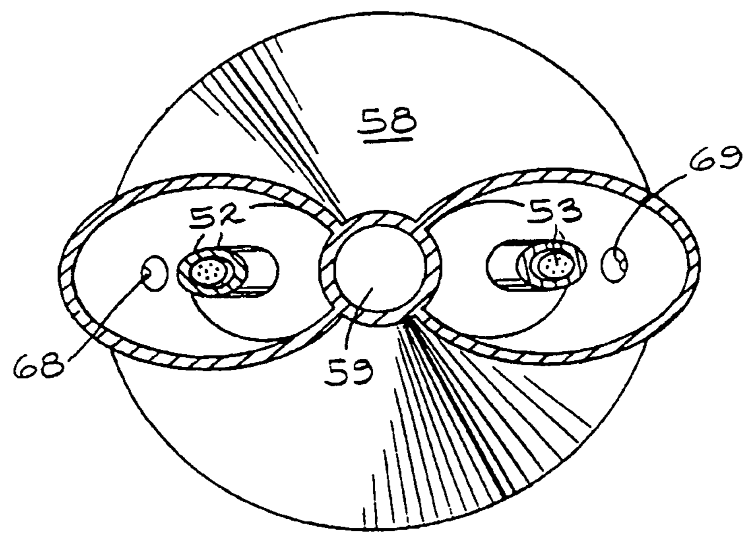
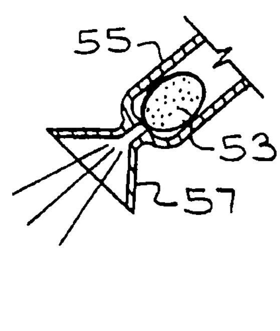


FIG. 4A

FIG. 4B



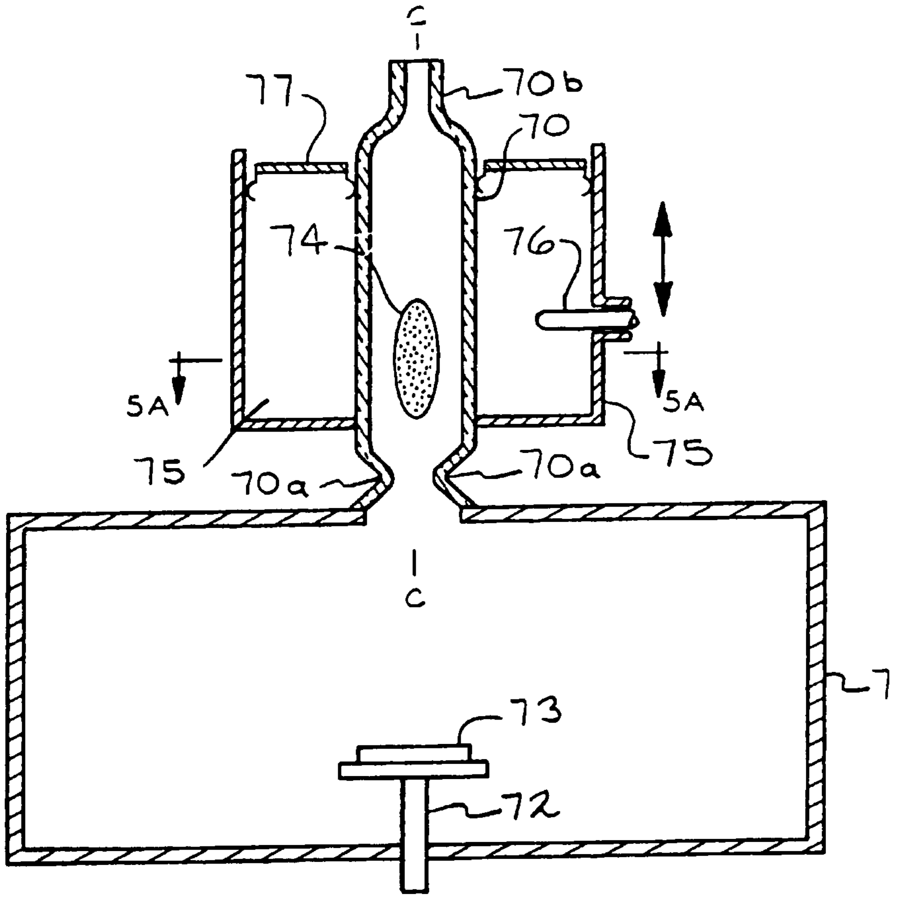


FIG. 5

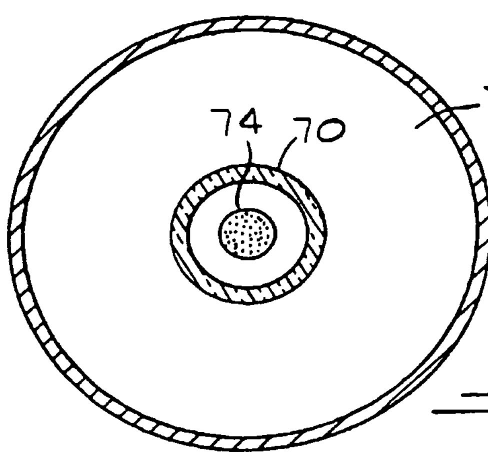


FIG. 5A

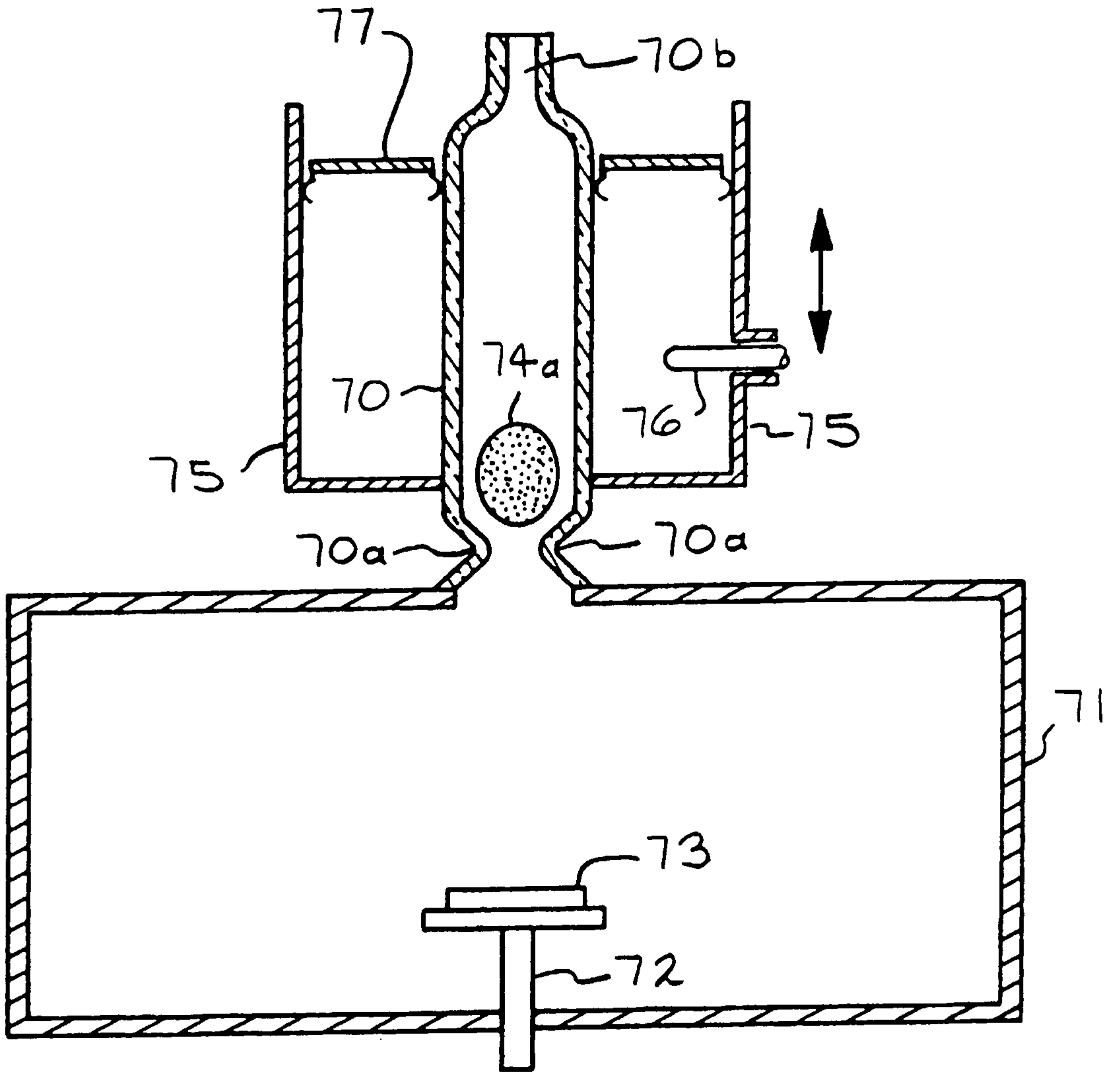


FIG. 5B

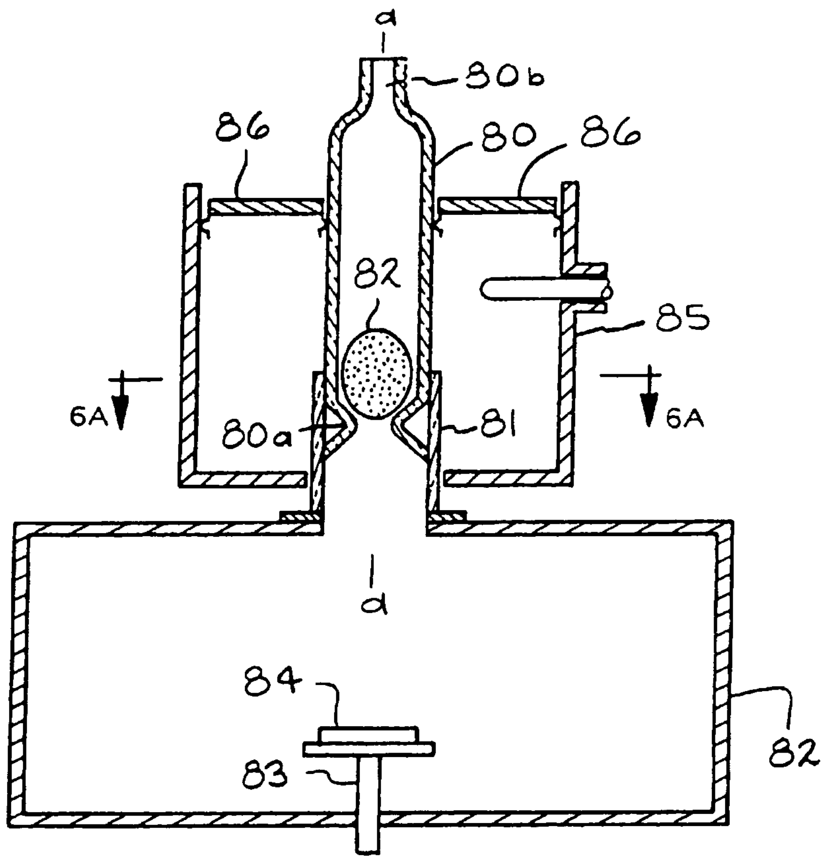


FIG. 6

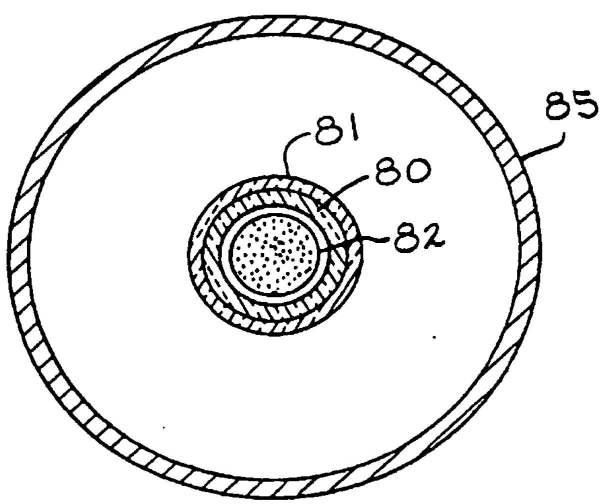


FIG. 6A

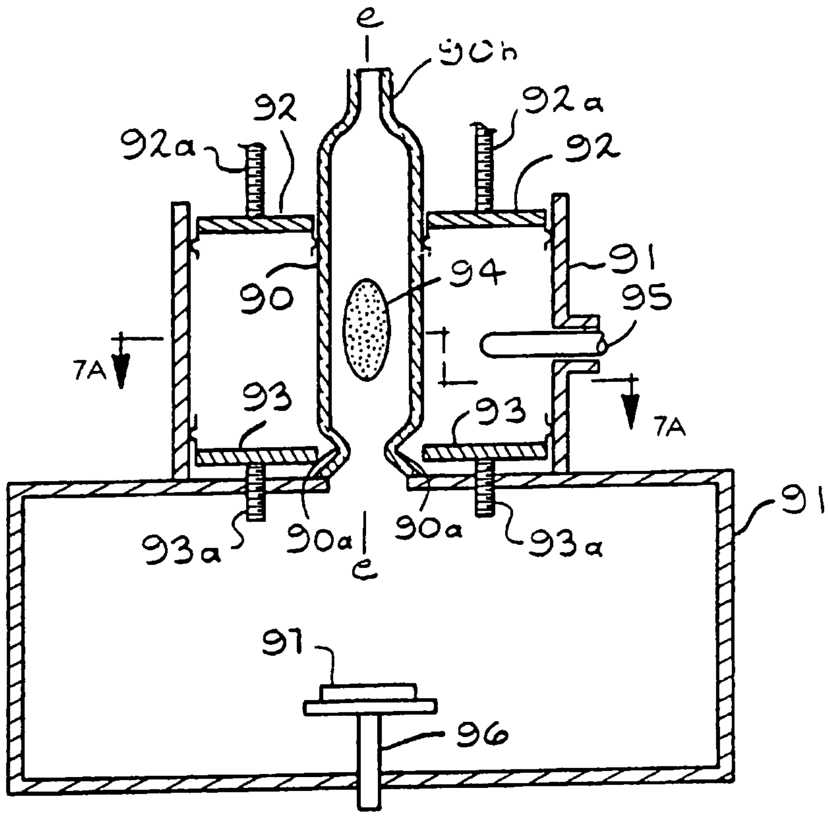

e
90h
92
92a
92a
92
91
94
90
95
7A
93
93
7A
91
93a
90a
e
90a
93a
91
96

FIG. 7

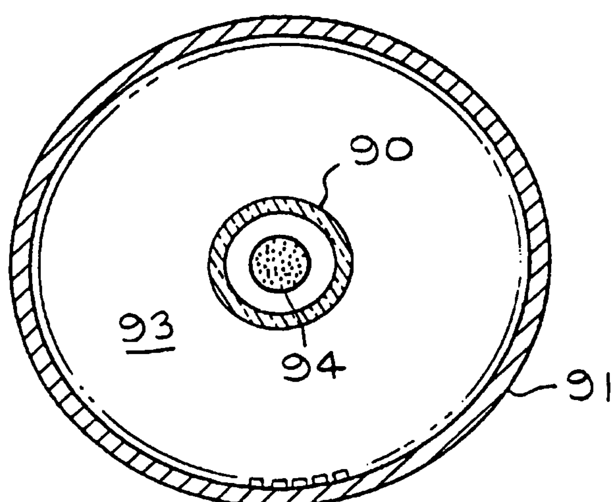

90
93
94
91

FIG. 7A